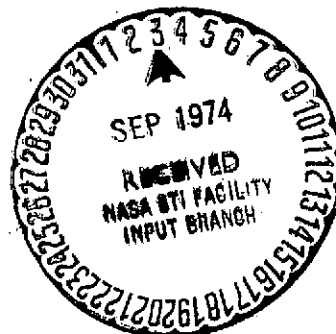


**NASA TECHNICAL  
MEMORANDUM**

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**ADVANCED RANKINE AND BRAYTON CYCLE POWER SYSTEMS:  
MATERIALS NEEDS AND OPPORTUNITIES**

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## ABSTRACT

Conceptual advanced potassium Rankine and closed Brayton power conversion cycles offer the potential for improved efficiency over steam systems through higher operating temperatures. However, for utility service of at least 100, 000 hours, materials technology advances will be needed for such high temperature systems. Improved alloys and surface protection must be developed and demonstrated to resist coal combustion gases as well as potassium corrosion or helium surface degradation at high temperatures. Extensions in fabrication technology are necessary to produce large components of high temperature alloys. Long time property data must be obtained under environments of interest to assure high component reliability.

# ADVANCED RANKINE AND BRAYTON CYCLE POWER SYSTEMS: MATERIALS NEEDS AND OPPORTUNITIES

S. J. Grisaffe and D. C. Guentert

Lewis Research Center

## SUMMARY

Current steam power plants operate at conversion efficiencies of nearly forty percent. By adding heat at higher temperatures, advanced Rankine and Brayton cycle concepts offer the possibility of increased efficiency, reduced fuel consumption per  $MW_e$ , and reduced waste heat rejection to the environment. Such systems may also offer improved plant siting flexibility. Two of the many advanced systems being examined are the potassium topping cycle and the closed Brayton cycle systems. Needs for the advanced materials technology to provide long lived, reliable components are discussed in terms of these systems.

In the potassium topping cycle system, fireside corrosion of the boiler tubes and corrosion/erosion of the boiler pressurizing system turbine will require improved alloys and surface protection systems. In addition, the tube interiors must also resist potassium (K) corrosion. The development of large, high temperature turbine disks and related fabrication technology may also be required.

In the closed Brayton system, coal fired units will also need resistance to fireside corrosion. For a helium working fluid, impurity effects on strength and high temperature surface depletion are of concern. Large tubular recuperators may also require improved materials if system temperatures are significantly increased to increase efficiency.

As systems are selected for continued development, there are real opportunities for tailoring materials to meet specific system needs. Fabrication technology advances are needed to produce large, multi-tubed boilers, turbine components, and recuperators with long lives. And, design data out to 10, 000 hours under environments of interest are also needed to assure high component reliability.

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## INTRODUCTION

At the request of several Federal agencies, the Lewis Research Center of NASA is assisting in the national effort to develop more efficient energy conversion systems having minimum environmental impact. In this regard, Lewis is drawing on a technology base built up over thirty years in the development of high efficiency aircraft and rocket propulsion systems and advanced space power systems. The purpose of this paper is to highlight some of the materials needs expected to exist as advanced ground power systems are: 1) better defined; 2) shown through demonstration of critical technology items to be ready for continued development; and 3) brought to pilot and demonstration plant status. To accomplish this purpose, primary consideration will be given to advanced Rankine and Brayton concepts; primarily the potassium topping and closed Brayton cycles. These systems were selected for discussion because they exemplify a range of materials needs and are illustrative of the opportunities that exist for developing the necessary materials technology in phase with a specific system development. However, these systems, along with the other candidate conversion systems, will require further study before their relative merits can be fully assessed.

## BACKGROUND

During this century power plants based on the steam Rankine cycle have been steadily developed and improved. A modern steam plant converts fossil fuel energy into electricity at about 40 percent efficiency. Thus, of 100 megawatts (MW) of energy in fuel burned to produce steam, 40 megawatts of electricity ( $MW_e$ ) are introduced into the electrical power grid and 60 MW are lost as waste heat. The growing national interest in advanced power systems stems from a desire to conserve (and extend) fossil fuel reserves as well as to

minimize the impact of growing electrical energy production on the environment. As shown in figure 1, by increasing conversion efficiency 10 percentage points, i. e. from 40 to 50 percent, a saving of 20 percent can be achieved in fuel consumption per  $MW_e$  with consequent benefit to the national energy supply and to the environment as a result of the reduced fuel burned (and thus fewer combustion products generated). Similarly, the rejection of waste heat per  $MW_e$  to the environment is decreased by 33 percent.

A number of advanced fossil fueled conversion systems are currently being proposed for stationary power applications. These include high temperature open cycle gas turbine systems, recuperated and unrecuperated; the combined gas turbine/steam cycle; the supercritical  $CO_2$  cycle; magnetohydrodynamic systems (MHD); and the liquid metal topping cycles for steam. All of these systems must meet the goals of high efficiency and low pollution. Long life and high reliability commensurate with electric utility requirements (100, 000 to 280, 000 hours) are also required with the possibility of rapid, economical replacement of critical components having shorter lives. It is necessary that the advanced conversion systems also be competitive with current systems in total costs of producing electricity including capital, operating, and maintenance costs. To achieve the optimum combination of performance and cost, such advanced systems are expected to operate at higher temperatures and stresses and in more adverse environments than present power plants. This combination of demands will require advances in materials technology in a number of areas.

The potential operating life of a conceptual power conversion system is a very important consideration in its selection for continued development. There are many factors which can influence conversion system component life. For example, figure 2 (ref. 1) shows the factors which influence gas turbine blade life. Similar curves can be considered for any power system component since the causes of failure can vary depending on the specific realm of operation. Mechanical fatigue at lower temperatures and creep at higher temperatures are generally the ultimate controllers of material and component life.

However, environmental effects such as oxidation and hot corrosion as well as operational effects such as cycle frequency and thermal transients can greatly reduce potential life. For these reasons, materials characterization under conditions closely approximating service will be needed to assure designers that a material property data base exists which is appropriate for component design and life estimation. For example, to develop the needed material property data base, test data for times of at least 10, 000 hours at temperature are needed for steady state behavior (creep and rupture), combined with cyclic test data for times of 1, 000 hours in order to extrapolate to material use times of at least 100 000 hours. Such long time test data are needed on most current materials as well as on any new materials which will be developed specifically for the power industry. These data will assure confidence in and provide verification for extended life prediction and design techniques.

Materials improvements can contribute significantly toward increasing conversion system performance as well as life. Figure 3 (ref. 2) traces the increase in turbine blade material temperature with time over the last 25 years. Note that around 1960 the strength increases achieved by decreasing chromium and increasing refractory metal content permitted use temperatures where oxidation/corrosion instead of strength became life limiting. The materials advances shown in figure 3, illustrate the continuing effort to develop alloys specifically designed for new aircraft engines. The successes of tailoring composition to application, combined with advances in turbine cooling technology, are reflected in the growth of aircraft gas turbine engine thrust from near 18, 000 to over 40, 000 lbs during this time with accompanying decreases in specific fuel consumption and specific engine weight. Thus, to improve power system performance, there are opportunities for tailoring materials for specific life and service requirements.

#### POTASSIUM TOPPING CYCLE

Modern steam plants with efficiencies approaching 40 percent are now near the economic limits of efficiency improvement. The gain in

efficiency that could be obtained by increasing steam temperature above current values is relatively small because of the thermodynamic properties of steam. Thus, it may not be economical to raise steam temperatures by the use of more expensive, higher temperature alloys in the very large steam boilers.

The possibility of using potassium as a working fluid in a Rankine cycle "on top of" steam was established through the research and technology efforts in support of advanced space power systems by NASA and other government agencies. Figure 4 shows a temperature-entropy diagram for such a system in which the waste heat from the potassium system is used to power a steam plant. The improvement in efficiency of the potassium topping system over the steam plant alone results from the greatly increased average temperature at which energy is added to the potassium system. Another benefit is that the pressure of the potassium vapor at such high temperatures is only a small fraction of steam pressures in conventional boilers.

A conceptual design study, sponsored jointly by NASA and OCR, has been conducted for a commercial sized (1200 MW) potassium (K) topping cycle power plant (Rossbach, R. J.: Study of Potassium Topping Cycles for Stationary Power. GE SP-741, NAS 3-17354, to be published). This study indicated a potential conversion efficiency of 50 percent or more with a potassium turbine inlet temperature of at least  $760^{\circ}\text{C}$ . A simplified schematic diagram for such a system is shown in figure 5. A pressurized boiler (10-15 ATM) generates potassium (K) vapor at about  $760^{\circ}\text{C}$  and 1 ATM. Electricity is generated by the boiler pressurizing system turbine and the potassium turbine. The K turbine exhaust enters a heat exchanger where additional energy is removed through a "conventional" steam cycle system which also generates electricity. Material needs appear to exist in the K boiler, the K turbine, and in the boiler pressurizing system turbine. (Much of the technology for the K/steam heat exchanger, also considered an area of materials and fabrication technology need, is expected to be derived from work on the Liquid Metal Fast Breeder Reactor which involves a similar sodium/steam heat exchanger).

## Potassium Boiler

Under the initial concept study by Rossbach, two modular K boiler concepts appeared worthy of further consideration. Modules of each concept are shown schematically in figures 6 and 7. A coal-derived low Btu gas fired pressurized boiler concept (fig. 6) offered a natural extension of current marine boiler technology. Operating at pressures to 15 ATM, flame temperatures to  $1590^{\circ}\text{C}$  would be developed burning "clean fuel". The high gas temperatures and pressures promise high heat transfer rates and thus significant size reductions compared to conventional steam boiler technology. The combustion of "clean fuel" is expected to minimize any fireside corrosion of the boiler tubes compared to direct combustion of coal at similar flame temperatures. While the conversion efficiency was estimated to be over 50 percent, the need for coal derived clean fuel (provided at about an 80 percent conversion efficiency from coal) somewhat lowered the total performance benefits of this approach. Note that the initial design called for 2200 tubes in one boiler module (eight modules per plant) while each tube is proposed to be more than six meters (20 feet) long.

The second concept - a pressurized fluidized bed boiler - (fig. 7) has a much smaller technology base but because coal is burned directly, it is of greater potential interest in that the full 50 percent or more efficiency can be achieved. Because coal combustion in the fluidized bed takes place at temperatures near  $900^{\circ}\text{C}$  (below the ash fusion temperature), liquid slag deposits, which generally produce the severest form of fireside corrosion, are not expected to develop. The low combustion temperature is also expected to minimize  $\text{NO}_x$  while the presence of limestone or dolomite in the bed will allow the burning of higher sulfur coal. The tube materials initially proposed for these boilers include HS-188, a wrought cobalt alloy; Inco 617, a wrought nickel alloy, - both of which cost several dollars per pound -; and in cooler regions, 304 stainless steel which costs over a dollar per pound. Tube walls 0.07 - 0.2 cm (30 to 80 mils) were considered.

The combined possibilities of fireside corrosion (tube surface) and potassium corrosion (inside tube) exist in such boiler tubes and



become more critical as thinner walls are considered to minimize cost. For such corrosion, little long time data exist for the materials of interest. Figure 8 presents some of the only "long time" pressurized fluidized bed materials corrosion test data generated to date (ref. 3). The 688° C data on 316 stainless steel show low effective thickness losses in 1000 hours - the maximum test time. However, it is risky to attempt to extrapolate such data over two orders of magnitude in time for several reasons. First, the data represent conversions from weight change data and assume uniform surface losses. Maximum depth of attack is a more real indication of loss of useful cross section (load carrying ability). Second, the corrosion mechanisms and attack rates are time dependent. In many reported cases of hot corrosion, a low initial rate was followed by rapid, catastrophic attack.

At the higher potential metal temperatures, which could eventually approach 900° C, increased fireside corrosion can be expected. If sodium chloride is added to the bed, as some sources have suggested, to regenerate the limestone in situ, increased attack is assured. To clearly identify the current state of technology, long time evaluation under realistic fluidized bed conditions is needed. The potential for further improving performance through increased operating temperature (but still within the range where sulfur removal by the limestone is satisfactory i.e. to about 960° C) need for the development of advanced high temperature, more corrosion resistant tubing alloys. In addition, there is a very good chance that highly effective and yet low cost surface protection systems will also be required to further extend tubing life.

Such tubing developments must not ignore the potential K corrosion possibilities which exist on the tube interiors. Again, no systematic data base exists on K corrosion at times much beyond 5,000 hours and on many of the potential tube materials. Some general K corrosion data on 316 stainless steel at 860° C, in figure 9, indicate that this material is near its long time upper temperature limit (ref. 4), but lower temperatures, more commensurate with long time properties for this material, can be expected to be less harmful. The combined effects of general attack, surface depletion of critical elements by dissolution in the K, and grain boundary or localized penetration must

be established for potential tube alloys. Exposure to two phased flow is necessary to simulate the service environment since at the boiling interface the corrosion problem is expected to be most severe. Only when demonstrated K corrosion resistance is coupled with fireside corrosion resistance in the same material system can the boiler tube technology for the K topping cycle be viewed as ready for advanced development. Clad or coated tubing could help this occur.

The multitude of tubes and joints in both K boiler concepts clearly indicated a need for the development of optimized low cost tube joining technology supported by non-destructive evaluation techniques to guarantee a no-leak system.

### Pressurizing System Turbine

When operating on the combustion gases from a pressurized boiler burning "clean fuel", the problem of the pressurizing turbine should be similar to those of current aircraft and naval gas turbines depending on how "clean" the available fuels are. When operating on the combustion products from a coal burning fluidized bed, a gas turbine may experience not only hot corrosion but the additional problems of particle erosion due to carry-over from the bed, and perhaps the formation of deposits of combustion products/bed constituents on the turbine airfoils which could reduce aerodynamic efficiency. That hot corrosion must be avoided can be clearly seen from the damage visible on an aircraft gas turbine vane component (fig. 10) after the engine was operated in a marine air environment. There is considerable effort now underway by the aircraft engine companies, the military, and NASA-Lewis to minimize such hot corrosion. These studies should directly benefit the pressurizing system turbine development effort. An example of progress in this area is shown in figure 11 which compares the performance of a Lewis RC developed duplex NiCrAlSi alloy plus surface aluminide coating to that of a commercial aluminide coating after 200 hours in an accelerated hot corrosion test. Figure 12 (ref. 5) indicates that fuel additives may also decrease hot corrosion of high strength turbine alloys. However, only when the performance of the potential turbine component materials of interest is evaluated in the specific combustion gas, etc. environments, can the true severity of the materials problems in the pressurizing system turbine

the specific combustion gas, etc. environments, can the ture severity of the materials problems in the pressurizing system turbine be resolved.

### Potassium Turbine

Earlier work with small potassium turbines (approx. 25 cm - 10 in. dia) for space power provided some confidence in the ability to design and operate larger K turbines. Figure 13 (ref. 6) shows such a turbine operated with both superalloy (U-700) and molybdenum alloy (TZM) blades. After 4300 hours at an inlet temperature of  $755^{\circ}\text{C}$  (about that near the lower temperature considered for potassium topping cycle turbine operation) only minor attack was observed. The effects of longer test times still require evaluation.

The K turbine disk technology may also require extension. Table I compares the size requirements, and the limits of current aircraft turbine disks with those conceived for the potassium topping cycle disk. Since present concepts do not include disk cooling, disk rim temperatures could approach  $760^{\circ}\text{C}$ . For the very long times anticipated (unless programmed component replacement is cost effective) the disk would be required to operate near the strength limits of the best current disk alloys such as Astroloy and could be in a creep life limited condition. Improved creep resistance of disk materials may be needed. Secondly, if cost or design trade-off studies indicate that it is desirable to minimize the number of turbine stages or eliminate the need for multiple turbines, then large disks, to 200 cm (80 in.) diameter could be required. The ability to forge such large components of high strength, high temperature alloys is beyond the limits of current direct forging technology. (Industrial gas turbines incorporate disks to approx. 150 cm (60 in.) but are made of easier to forge alloys). If even higher temperatures are eventually needed to improve the cost-effectiveness of the K topping cycle, the possibility could arise where molybdenum alloy TZM disks might be considered. However, major processing advances would be necessary before serious consideration of this possibility could even be entertained.

## THE CLOSED BRAYTON CYCLE

The closed Brayton cycle is another concept of interest for stationary power generation. This cycle incorporates high internal gas pressures and thus permits compact conversion system components. Because the cycle rejects heat over a wider range of temperatures than the steam cycle, it lends itself more readily to the use of smaller, dry cooling towers than does a condensing cycle and so has an advantage in siting flexibility.

A number of fossil fueled closed Brayton cycle systems are now operating in Europe in applications where the cycle waste heat is used for process heat or for district heating. Such total energy systems can achieve overall energy efficiencies as high as 70 to 80 percent. In these systems air is used as the working fluid at relatively modest turbine inlet temperatures - around  $700^{\circ}\text{C}$ . An interesting system using a combined open and closed Brayton cycle as a topping cycle for steam (similar to the K topping cycle) is shown in figure 14 (ref. 7). Like the potassium Rankine system a wide variety of fuels and energy sources can be used. If coal is burned directly, successful operation of the pressurizing system gas turbine operating on the products of a coal burning fluidized bed is mandatory. Long time oxidation of the air heater tubes and their ability to operate at the anticipated high pressures will also influence the attractiveness of this concept.

A closed Brayton cycle, using helium as the working fluid, is uniquely suited to integration with the high temperature gas cooled reactor (HTGR). A schematic of the HTGR-closed brayton power generation concept now in the preliminary design phase at General Atomics under contract to the AEC (ref. 8) is shown in figure 15. It is expected that the turbine inlet temperature can eventually be increased from  $815^{\circ}\text{C}$  to near  $1,000^{\circ}\text{C}$  in advanced designs and thus result in an increased conversion efficiency above 40 percent.

### Turbine

At current proposed turbine inlet temperatures near  $815^{\circ}\text{C}$ , there is concern for the surface stability of materials in impure helium. As

turbine inlet temperatures are increased to near  $1000^{\circ}\text{C}$  for improved efficiency. The effects of impurities in the helium on the turbine materials could be severe. The fact that impure helium can degrade rupture strength has been amply shown. Figure 16 (ref. 9) illustrates the specific degradation of impure helium on the  $750^{\circ}\text{C}$  rupture behavior of 316 stainless steel. Decreases of 15 percent in rupture strength, 50 percent in creep life, and crack growth rates several times those in air were reported. In the closed Brayton concept, much purer helium is expected. Still, low oxygen partial pressures can lead to internal oxidation and unexpected local surface instability - especially in alloys rich in reactive metals, i. e., chromium (Cr), titanium (Ti), zirconium (Zr), niobium (Nb), etc. The extent of such degradation is currently under evaluation by several organizations in support of the various HTGR concepts such as the Dragon Experimental Reactor Project. It can be expected that new alloys, specifically developed for helium service, can extend the useful lives of components in the current range of temperature interest. Based on the work of Sekino (ref. 10), it can be deduced that for higher temperature use, superalloys will probably not contain much Cr. As figure 17 from that reference shows, at  $1000^{\circ}\text{C}$  (near the high temperature end of the potential close Brayton cycle operating range) Cr depletion in 600 hours was severe for common wrought alloys Hastelloy X, Incoloy 800, and Inco 617 which contain approx. 15 - 20 percent Cr. If chromium is found to be necessary for other considerations, however, ref. 10 also indicated that preoxidation and pack aluminization coating could serve to minimize surface attack. Thus, new alloys and even protective coatings based on extensions of current technology or on radically different compositions appear worthy of further consideration.

### Heat Exchangers

The closed Brayton cycle concept generally includes a recuperator to improve cycle efficiency. For stationary power applications, recuperators will probably have to be of tubular construction to withstand the high working pressures. Further, a modular approach may be

necessary to limit unit size so as to allow factory fabrication and rail shipment whenever possible. A schematic diagram of the HTGR-closed Brayton system recuperator design concept is shown in figure 18 (ref. 8). For this initial design, the hot gas inlet temperature is near  $540^{\circ}\text{C}$  and conventional  $2\frac{1}{4}\text{ Cr} - 1\text{ Mo}$  steel is being considered for the tubing. The number and size of the tubes, and the IR resulting total surface area and weight is rather impressive. Increases in turbine inlet temperatures, with corresponding increases in recuperator inlet temperature, may lead to the need for new tube alloys - probably superalloy types - which would result in increase consumption of costly and potentially critical elements such as cobalt, chromium, nickel, etc. Again, such new tube alloys will have to be specifically developed for helium service and for higher strength at temperature to foster reduced wall thickness. Thermal strain accomodation is also a significant problem in large multi-tube, multi-joint heat exchangers. Thus, advances in alloy, joining, and design technology appear necessary to provide large, high temperature/pressure heat exchangers with long service lives.

### CONCLUDING REMARKS

Advanced power systems appear desirable to achieve increased energy conversion efficiency and to reduce the environmental impact of increased power generation. Such systems will operate at higher temperatures, pressures and/or in more severe environments. At the same time, such systems will be expected to produce electricity at total costs near those of current systems and to be able to function in base-load service for lifetimes of 100,000 hours or more. Based on an examination of two selected advanced conversion systems under consideration - the potassium topping cycle and the closed Brayton cycle - several general areas can be identified which need improvements in materials technology.

Materials with combined resistance not only to air and to the combustion products of coal and coal derived fuels, but also to potassium vapor, helium containing impurities, and other potential working fluids, will be needed before advanced systems can be expected to

achieve utility life requirements. Such resistance must be demonstrated for long times under realistic environmental conditions and must be supported by long time property data (to  $10^4$  hours) to provide a basis for component designs and life prediction. In many cases, materials will have to be developed specifically for critical service requirements. And, low cost fabrication and NDE will be required to economically produce and assemble highly reliable large, complex components. Based on the history of aircraft turbine engine development, such materials efforts may well become a pacing element in the development and efficiency improvements of advanced ground electrical power systems.

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TABLE I. - TURBINE DISK TECHNOLOGY

Present Aircraft Disk Technology		K Turbine Concept Disk Needs
Size	To approx. 77 cm (30 in.)	To approx. 200 cm (80 in.)
Operating temperature	$T_{\max} \sim 540^{\circ} - 650^{\circ} \text{ C}$ , air cooled	$T_{\max} \sim 760^{\circ} \text{ C}$ , uncooled
Life	To $\sim 20,000$ hours max.	$> 30,000$ hours
Life limited by:	Generally, fatigue	Probably creep
Fabrication	Forging	Not yet determined-size and material dependent

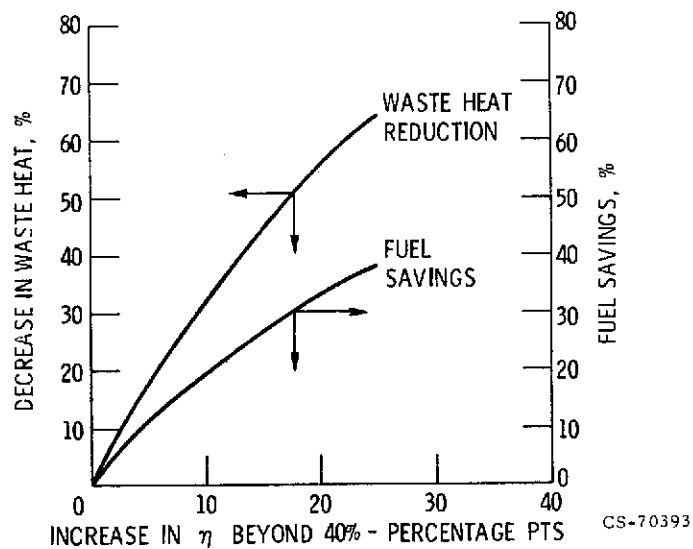


Figure 1. - Benefits of higher conversion efficiency,  $\eta$ .

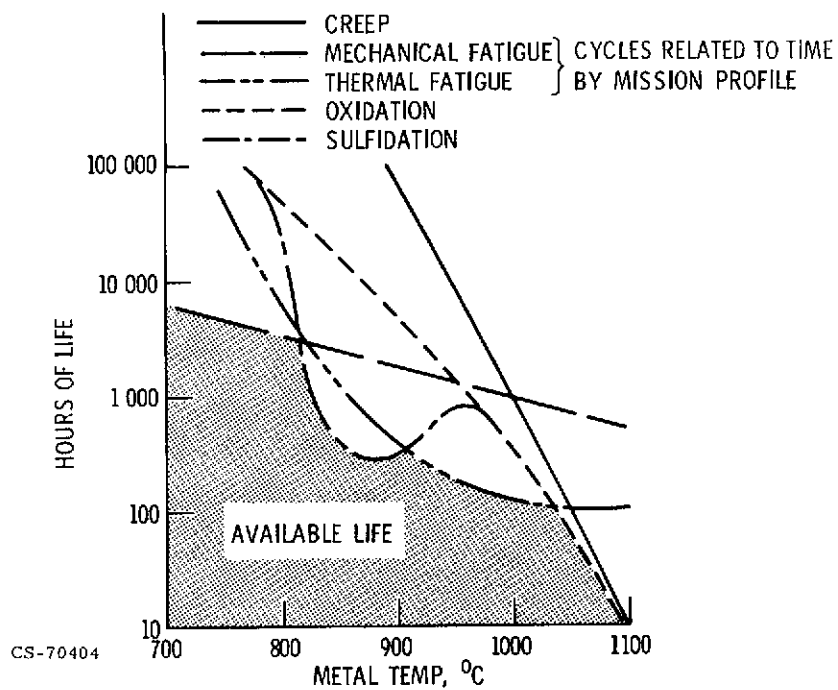


Figure 2. - Factors influencing turbine blade life (ref. 1).

# 1000-HR STRESS RUPTURE AT $13.8 \text{ MN/M}^2$ (20 KSI)

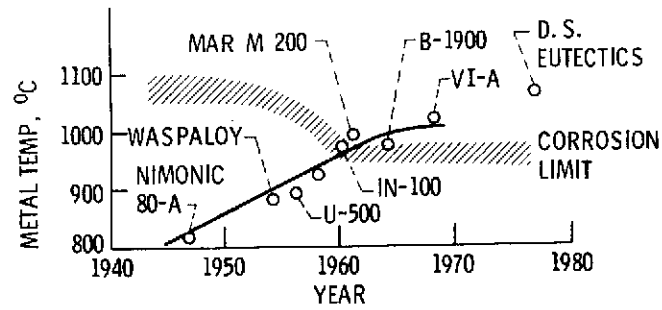


Figure 3. - Effect of improved alloys on turbine blade metal temperature and corrosion limit (ref. 2).

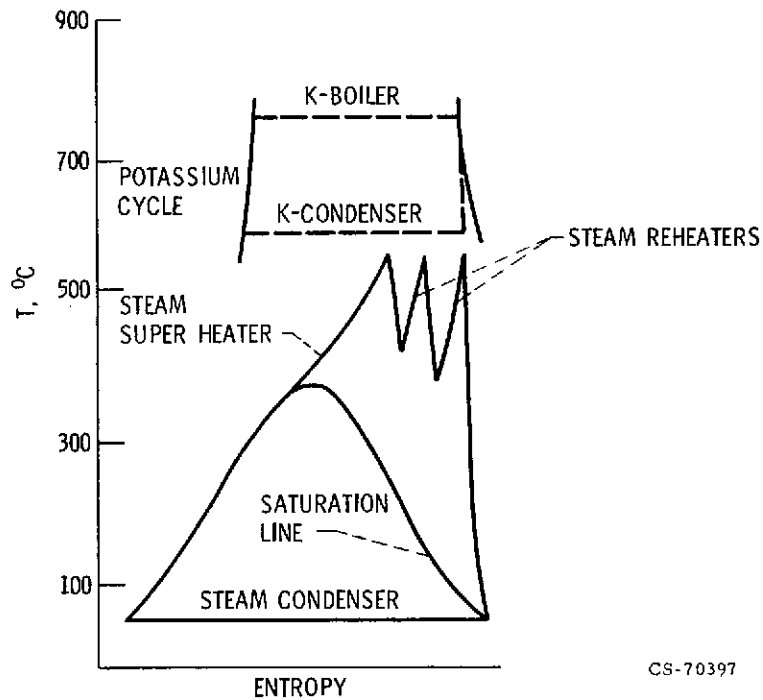


Figure 4. - Potassium topping cycle T-S diagram.

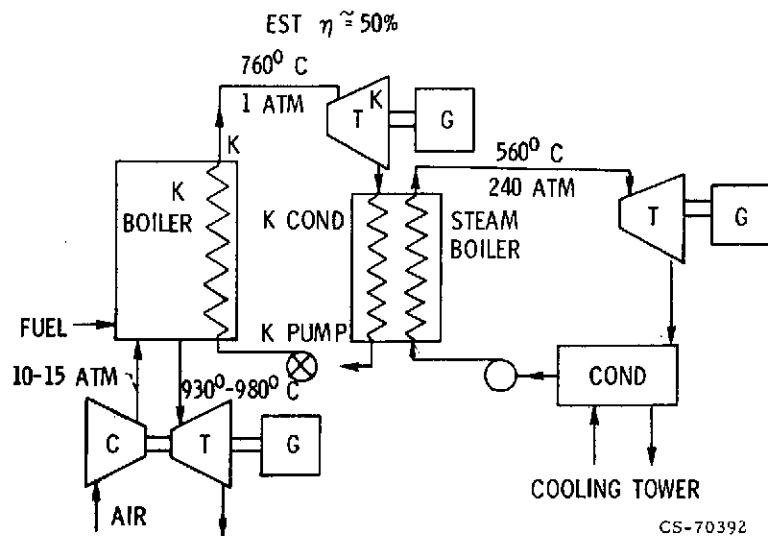


Figure 5. - Schematic of K topping cycle.

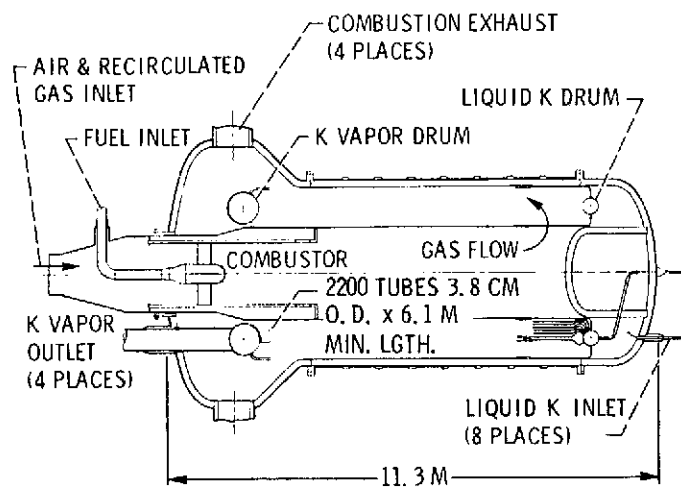


Figure 6. - Pressurized potassium boiler (8 required, ref. Rossbach.)

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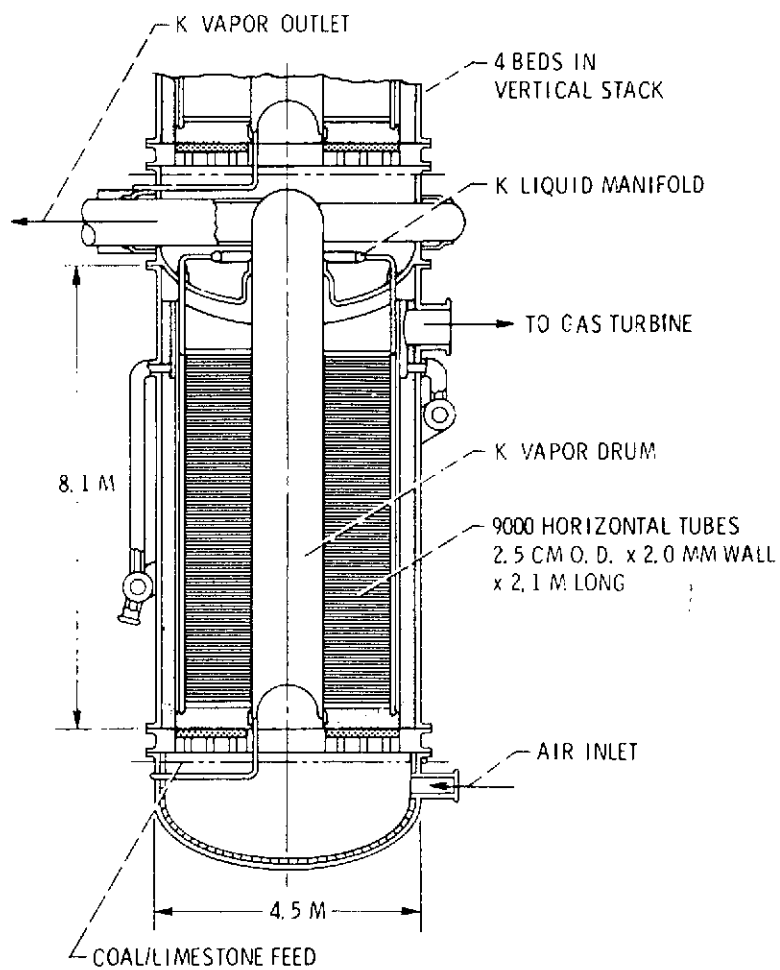


Figure 7. - Pressurized fluidized bed boiler (ref. Rossbach).

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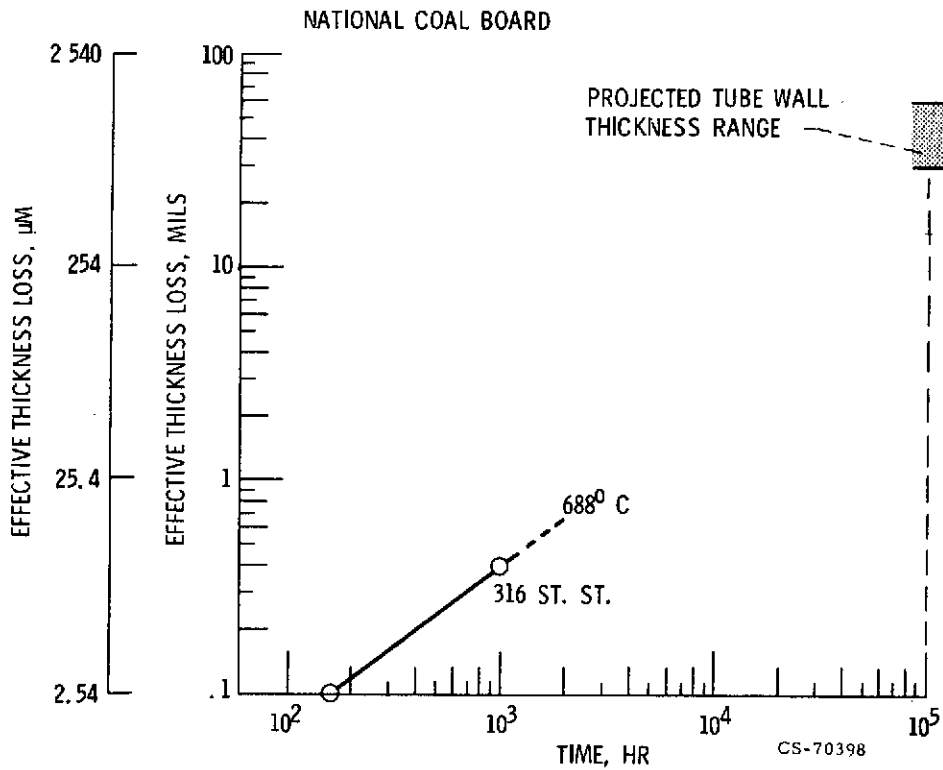


Figure 8. - Fluidized bed corrosion data.

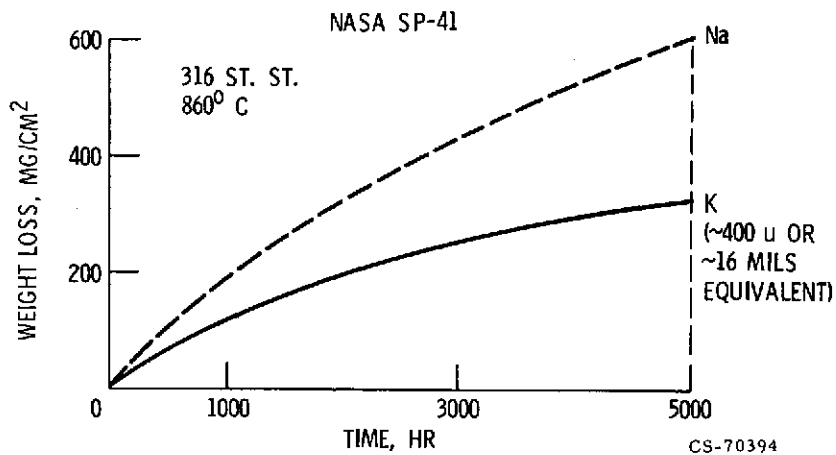


Figure 9. - General corrosion of tabs in liquid metal convection loops (ref. 4).

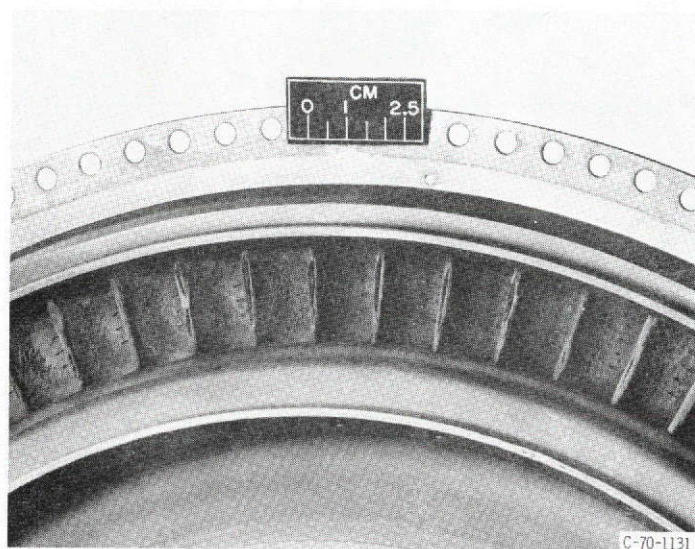
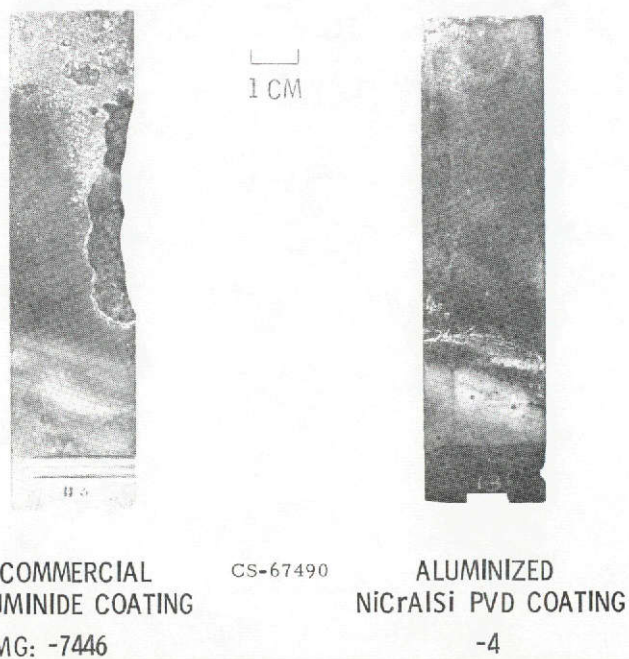


Figure 10. - Hot corrosion on aircraft turbine stator vanes operated in a marine environment.



AFTER 200-HR TEST & WATER SOLUBLE DEPOSITS REMOVED

Figure 11. - Aluminized Ni Cr Al Si and commercial aluminide coated IN-100 after sonic burner hot corrosion tests. Temperature, 900° C; sea salt, 5ppm; cyclic exposures, 1 hr; fuel, jet A-1 (0.04 percent S).

REF U. S. PATENT 3, 581, 491

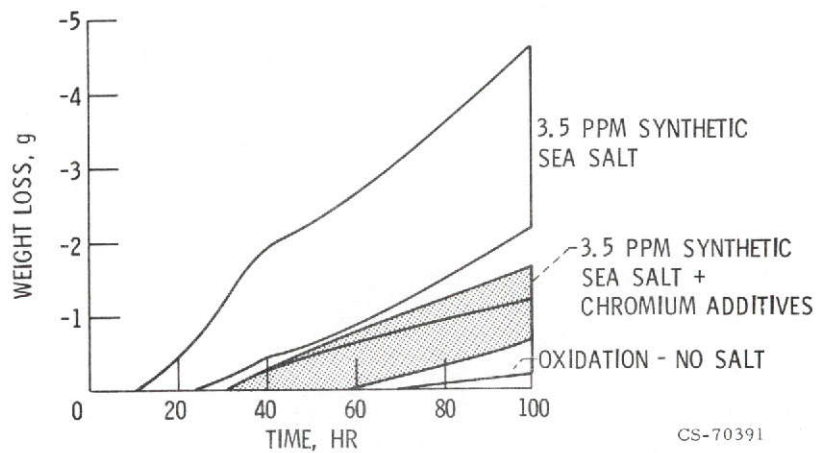


Figure 12. - Vane cyclic oxidation-erosion-sulfidation of uncoated B-1900 alloy (ref. 5).

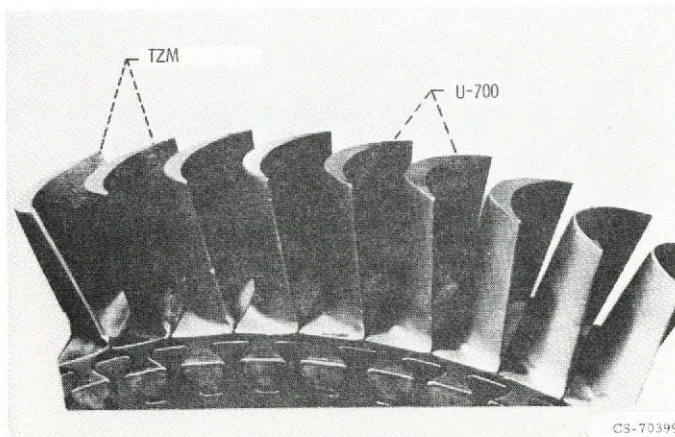
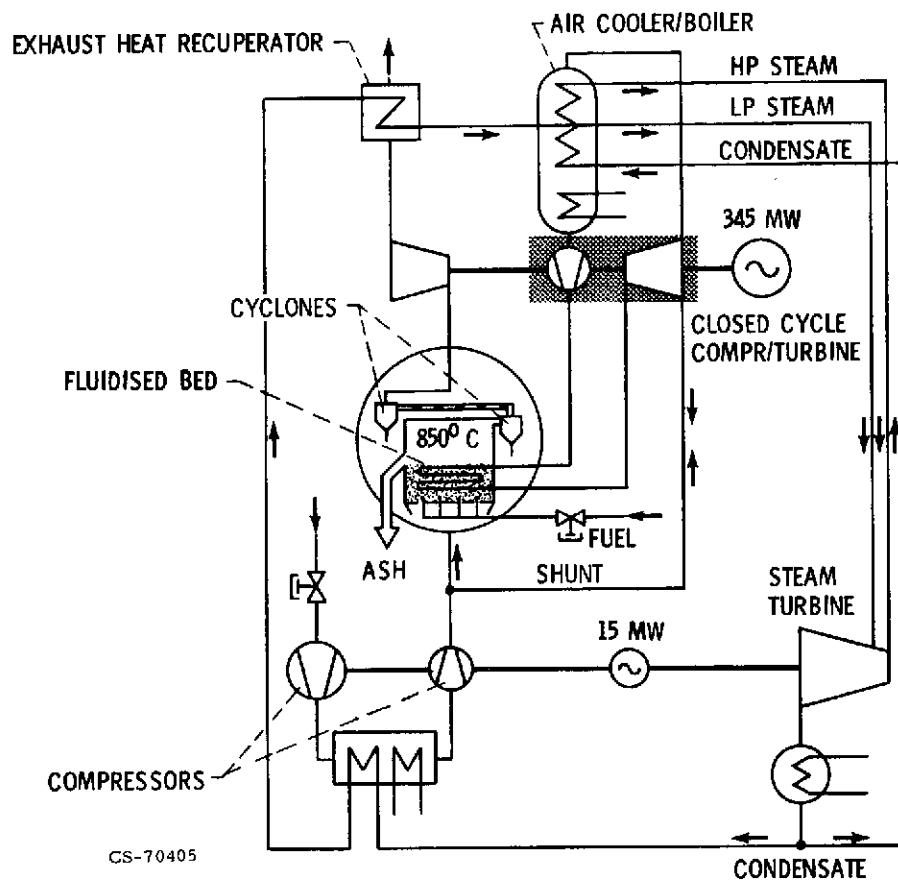


Figure 13. - Experimental space power system potassium turbine after 4300 hours of testing at an inlet temperature of 755<sup>0</sup> C (ref. 6).





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Figure 14. - Conceptual fossil-fueled closed Brayton cycle (ref. 7).

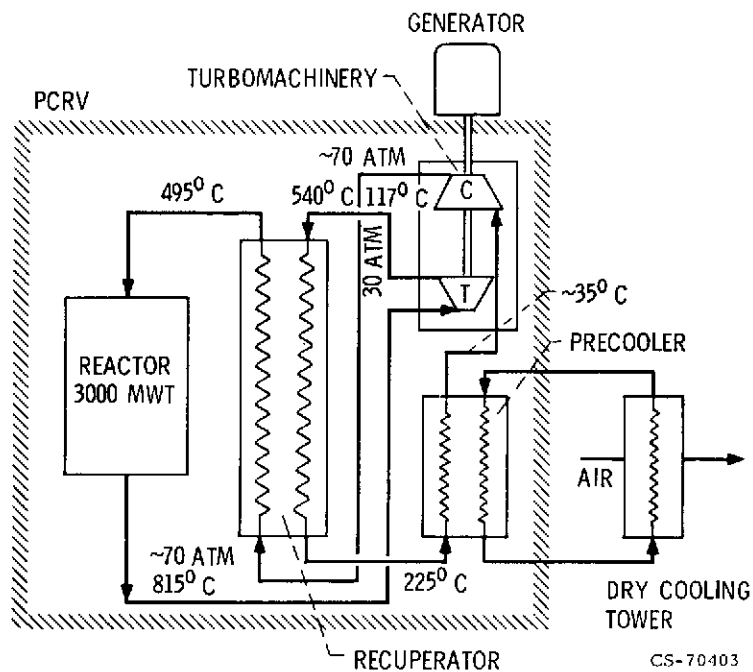


Figure 15. - Conceptual high temperature gas reactor (HTGR)-helium gas turbine cycle (ref. 8).

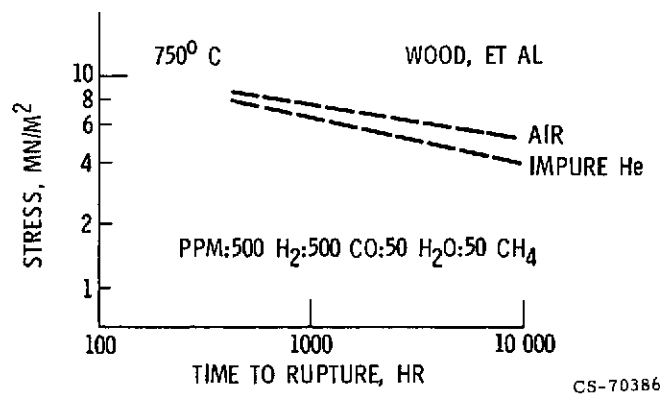


Figure 16. - A comparison of the rupture properties of 316 st. st. in impure helium and air (ref. 9).

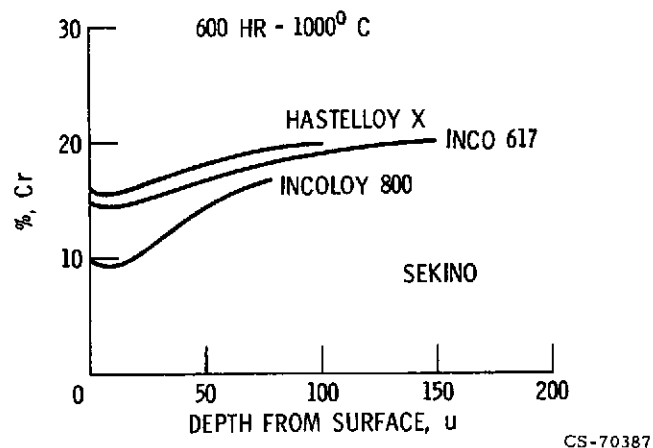


Figure 17. - Alloy surface depletion of chromium in 99.99% He (ref. 10).